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A novel stochastic fluid model is proposed with non-ideal structure factor consistent with compressibility, and adjustible transport coefficients. This Stochastic Hard Sphere Dynamics (SHSD) algorithm is a modification of the Direct Simulation Monte Carlo (DSMC) algorithm and has several computational advantages over event-driven hard-sphere molecular dynamics. Surprisingly, SHSD results in an equation of state and pair correlation function identical to that of a deterministic Hamiltonian system of penetrable spheres interacting with linear core pair potentials. The fluctuating hydrodynamic behavior of the SHSD fluid is verified for the Brownian motion of a nano-particle suspended in a compressible solvent.

With the increased interest in nano- and micro-fluidics, it has become necessary to develop tools for hydrodynamic calculations at the atomistic scale [1, 2]. Of particular interest is the modeling of flexible polymers in a flowing solvent for both biological (e.g., cell membranes) and engineering (e.g., micro-channel DNA arrays) applications. Typically the polymer chains are modeled using Molecular Dynamics (MD). For many applications, a realistic representation of the solvent and bidirectional coupling between the flow and the polymer motion is needed, for example, in the modeling of turbulent drag reduction. Previously, we introduced the Stochastic Event-Driven MD (SEDMD) algorithm that uses Direct Simulation Monte Carlo (DSMC) for the solvent coupled to deterministic EDMD for the polymer chain [3]. However, DSMC is limited to perfect gases. Efforts have been undertaken to develop solvents that have a *non-ideal* EOS, and that also have greater computational efficiency than brute-force molecular dynamics. Examples include the Lattice-Boltzmann (LB) method [4], Dissipative Particle Dynamics (DPD) [5], and Multi-Particle Collision Dynamics (MPCD) [6], each of which has its own advantages and disadvantages [1]. The *Stochastic Hard Sphere Dynamics* (SHSD) algorithm described in this Letter is based on successive stochastic collisions of variable hard-sphere diameters and is thermodynamically consistent (i.e., the direct calculation of compressibility from density fluctuations agrees with the density derivative of pressure). SHSD modifies previous algorithms for solving the Enskog kinetic equation [7, 8] while maintaining good efficiency.

In the SHSD algorithm randomly chosen pairs of approaching particles that lie less than a given diameter of each other undergo collisions as if they were hard spheres of diameter equal to their actual separation. The SHSD fluid is shown to be non-ideal, with structure and equation of state equivalent to that of a fluid mixture where spheres effectively interact with a repulsive linear core pairwise potential. We theoretically demonstrate this correspondence at low densities. Remarkably, we numerically find that this effective interaction potential, similar to the quadratic core potential used in many DPD variants, is valid at all densities.

The SHSD algorithm is not as efficient as DSMC at a comparable collision rate. However, when low compressibility is desired, SHSD is several times faster than EDMD for hard spheres, the fastest available deterministic alternative. Low compressibility, for example, is desirable so that flows are kept subsonic even for high Reynolds number flows. Furthermore, SHSD has several important advantages over EDMD, in addition to its simplicity:

- SHSD has several controllable parameters that can be used to change the transport coefficients and compressibility, while EDMD only has density.
- SHSD is time-driven rather than event-driven thus allowing for easy parallelization.
- SHSD can be more easily coupled to continuum hydrodynamic solvers, just like ideal-gas DSMC [9].

The standard DSMC [10] algorithm starts with a time step where particles are propagated advectively, $\mathbf{r}_i^{'} = \mathbf{r}_i + \mathbf{v}_i \Delta t$, and sorted into a grid of cells. Then, a certain number $N_{coll} \sim \Gamma_{sc} N_c (N_c - 1) \Delta t$ of *stochastic collisions* are executed between pairs of particles randomly chosen from the N_c particles inside the cell. The conservative stochastic collisions exchange momentum and energy between two particles i and j that is not correlated with the actual positions of the particles. Typically the probability of collision is made proportional to the magnitude of the relative velocity $v_r = |\mathbf{v}_{ij}|$ by using rejection. For mean free paths comparable to the cell size, the grid of cells should be shifted randomly before each collision step to ensure Galilean invariance. DSMC, unlike MD, is not isotropic and does not conserve angular momentum, leading to an anisotropic stress tensor. To avoid these cell artifacts, all collision partners within a collision diameter D must be considered even if they are in neighboring cells, with a suitable modification of the trial collision frequency to maintain the same collision rate as DSMC. This grid-free variant will be called

Isotropic DSMC (I-DSMC). The cost is that is the computational efficiency is reduced by a factor of $2-3$ due to the need to perform neighbor searches.

Because the collisional momentum exchange $m\Delta\mathbf{v}_{ij}$ in traditional DSMC is not correlated with the displacement $\Delta\mathbf{r}_{ij}$ between the colliding particles, the virial $\langle\Delta\mathbf{v}_{ij}\cdot\Delta\mathbf{r}_{ij}\rangle$ vanishes giving an ideal-gas pressure. In order to introduce a non-trivial equation of state it is necessary to either give an additional displacement to the particles that is parallel to $\Delta\mathbf{v}_{ij}$, or to bias the momentum exchange $\Delta\mathbf{v}_{ij}$ to be (statistically) aligned to $\Delta\mathbf{r}_{ij}$. The former approach has already been investigated in the Consistent Boltzmann Algorithm (CBA) [11]; however, CBA is not thermodynamically consistent since it modifies the compressibility without affecting the density fluctuations (i.e., the structure of the fluid is still that of a perfect gas). A fully consistent approach is to require that the particles collide as if they are elastic hard spheres of diameter equal to the distance between them at the time of the collision. Such collisions produce a positive virial only if the particles are approaching each other, $v_n = -\mathbf{v}_{ij}\cdot\hat{\mathbf{r}}_{ij} > 0$, therefore, we reject collisions among particles that are moving apart. Furthermore, as for hard spheres, it is necessary to collide pairs with probability that is *linear* in v_n, which requires a further increase of the rejection rate and thus decrease of the efficiency. The EOS of a fluid with no internal energy must be linear in temperature, which from the virial theorem $p_c \sim \langle\Delta\mathbf{v}_{ij}\cdot\Delta\mathbf{r}_{ij}\rangle_c \sim \Gamma_{sc}\sqrt{T_c}$ implies that the *local* collisional frequency Γ_{sc} must be proportional to the square root of the *local* temperature T_c, $\Gamma_{sc}\sim\sqrt{T_c}$, as for hard spheres. Without rejection based on v_n or v_r, temperature fluctuations would not be consistently coupled to the local pressure p_c because $p_c\sim\sqrt{T_c}$ instead of $p_c\sim T_c$. For DSMC the collisional rules can be manipulated arbitrarily to obtain the desired transport coefficients, however, for non-ideal fluids thermodynamics eliminates some of the freedom. Note that one can in fact mix SHSD collisions with I-DSMC collisions, that either take into account or ignore the v_n requirement, to introduce more tunable parameters in SHSD. The efficiency is significantly enhanced when the fraction of accepted collisions is increased, however, the compressibility is also increased at a comparable collision rate.

For sufficiently small time steps, the SHSD fluid can be considered as a simple modification of the standard hard-sphere fluid. Particles move ballistically in-between collisions. When two particles i and j are less than a diameter apart, $r_{ij}\le D$, there is a probability rate $(3\chi/D)v_n\Theta(v_n)$ for them to collide as if they were elastic hard spheres with a variable diameter $D_S = r_{ij}$. Here Θ is the Heaviside function, and χ is a dimensionless parameter determining the collision frequency. The prefactor $3/D$ has been chosen so that for an ideal gas the average collisional rate would be χ times larger than that of a low-density hard-sphere gas with density (volume fraction) $\phi = \pi N D^3/(6V)$.

In order to understand properties of the SHSD fluid as a function of ϕ and χ, we consider the equilibrium pair correlation function g_2 at low densities, where correlations higher than pairwise can be ignored. We consider the cloud of point walkers ij representing the $N(N-1)/2$ pairs of particles, each at position $\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$ and with velocity $\mathbf{v} = \mathbf{v}_i - \mathbf{v}_j$. At equilibrium, the distribution of the point walkers in phase space will be $f(\mathbf{v},\mathbf{r}) = f(v_r, r) \sim g_2(r)\exp(-mv_n^2/4kT)$. Inside the core $r < D$ this distribution of pair walkers satisfies a kinetic equation

$$\frac{\partial f}{\partial t} + v_n\frac{\partial f}{\partial r} = v_n\Gamma_0 f,$$

where $\Gamma_0 = 3\chi/D$ is the collision frequency. At equilibrium, $\partial f/\partial t = 0$ and v_n cancels, consistent with choosing collision probability linear in $|v_n|$. Thus $dg_2/dx = 3\chi g_2\Theta(1-x)$, with solution $g_2(x) = \exp[3\chi(x-1)]$ for $x\le 1$ and $g_2(x) = 1$ for $x > 1$, where $x = r/D$. Indeed, numerical experiments confirmed that at sufficiently low densities the equilibrium g_2 for the SHSD fluid has this exponential form inside the collision core.

This low density result is equivalent to $g_2^U = \exp[-U(r)/kT]$, where $U(r)/kT = 3\chi(1-x)\Theta(1-x)$ is an effective *linear core* pair potential similar to the quadratic core potential used in DPD. Remarkably, it was found *numerically* that this weakly-repulsive potential can predict exactly $g_2(x)$ at *all* liquid densities. Figure 1 shows a comparison between the pair correlation function of the SHSD fluid on one hand, and a Monte Carlo calculation using the linear core pair potential on the other, at several densities. Also shown is a numerical solution to the hyper-netted chain (HNC) integral equations for the linear core system. The excellent agreement at all densities permits the use of the HNC result in practical applications, notably the calculation of the transport coefficients.

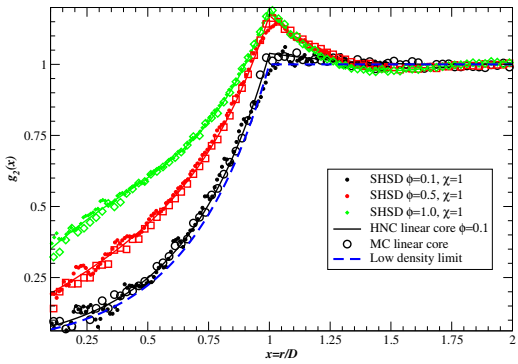

Figure 1: (Color online) Equilibrium pair correlation function of the SHSD fluid (solid symbols), compared to MC (open symbols) and HNC calculations (solid lines) for the linear core system, at various densities and $\chi = 1$.

An exact BBGKY-like hierarchy of Master equations for the s-particle distribution functions of the SHSD fluid is given in Ref. [12]. For the first equation of this BBGKY hierarchy, valid at low densities, we can neglect correlations other than pair ones and approximate $f_2(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2) =$

$g_2(\mathbf{r}_{12})f_1(\mathbf{r}_1,\mathbf{v}_1)f(\mathbf{r}_2,\mathbf{v}_2)$. With this assumption we obtain a stochastic Enskog equation similar to the revised Enskog equation for hard spheres but with a smeared distribution of hard-sphere diameters, as studied in Ref. [13]. The Chapman-Enskog expansion carried out in Ref. [13] produces the equation of state (EOS) $p = PV/NkT$, the self-diffusion coefficient ζ, the shear η and bulk η_B viscosities, and thermal conductivity κ of the SHSD fluid. The expressions ultimately give the transport coefficients in terms of various integer moments of $g_2(x)$, $x_k = \int_0^1 x^k g_2(x)dx$, specifically, $p-1 = 12\phi\chi x_3$, $\zeta/\zeta_0 = \sqrt{\pi}/(48\phi\chi x_2)$, $\eta_B/\eta_0 = 48\phi^2\chi x_4/\pi^{3/2}$, and

$$\eta/\eta_0 \text{ or } \kappa/\kappa_0 = \frac{c_1}{\sqrt{\pi}\chi x_2}(1+c_2\phi\chi x_3)^2 + c_3\eta_B/\eta_0,$$

where $\zeta_0 = D\sqrt{kT/m}$, $\eta_0 = D^{-2}\sqrt{mkT}$ and $\kappa_0 = kD^{-2}\sqrt{kT/m}$ are natural units, and $c_1 = 5/48$, $c_2 = 24/5$ and $c_3 = 3/5$ for η, while $c_1 = 25/64$, $c_2 = 24/5$ and $c_3 = 3/5$ for κ.

The above formula for the pressure is exact and is equivalent to the virial theorem for the linear core potential, and thus thermodynamic consistency between $g_2(x)$ and $p(\phi)$ is guaranteed. This stringent test of thermodynamic consistency that has been found difficult to satisfy in non-ideal variants of MPCD [6], which is essentially a variant of DSMC in which a sequence of binary collisions is replaced with a more efficient multi-particle collision [1, 14]. In the inset in the top part of Fig. 2, we directly demonstrate the thermodynamic consistency of SHSD by comparing the compressibility calculated from the EOS, $S_c = (p + \phi dp/d\phi)^{-1}$, to the structure factor at the origin $S_0 = S(\omega = 0, k = 0)$. Furthermore, good agreement is found between the adiabatic speed of sound $c_s^2 = S_0^{-1} + 2p^2/3$ and the location of the Brilloin lines in the dynamic structure factor $S(\omega; k)$ for small k values. In Fig. 2, we also compare the theoretical predictions for η utilizing the HNC approximation for g_2 to the ones directly calculated from SHSD. Surprisingly, good agreement is found for the shear viscosity at all densities. The corresponding results for ζ show significant ($\sim 25\%$) deviations for the self-diffusion coefficient at higher densities because of corrections due to higher-order correlations.

As an illustration of the hydrodynamic behavior of the SHSD fluid, we study the velocity autocorrelation function (VACF) $C(t) = \langle v_x(0)v_x(t)\rangle$ for a single neutrally-buoyant hard sphere of mass m and radius R suspended in an SHSD fluid of mass density ρ. This problem is relevant to the modeling of polymer chains in solution (where each bead in the chain is represented as a hard sphere) and to modeling (nano)colloidal suspensions, and has been studied extensively since the early days of MD when Wainwright and Alder discovered a long power-law tail in $C(t)$ [14, 15]. In our simulations the solvent-solvent particles interact via stochastic SHSD collisions. The solvent-solute interaction is treated as if the SHSD particles are hard spheres of diameter $D/4$ using an event-driven algorithm, as described

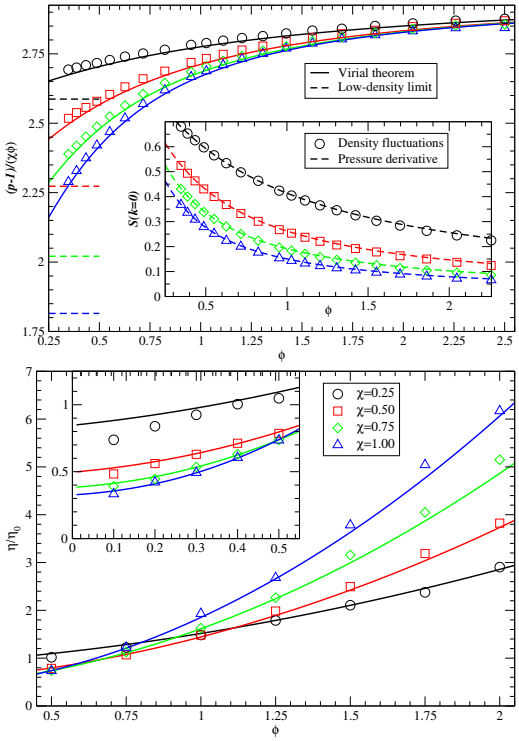

Figure 2: (Color online) (*Top*) Comparison of the equation of state $p(\phi)$ for SHSD at several collision frequencies (different symbols) with predictions based on the stochastic Enskog equation using the low-density $g_2(x)$ (dashed lines) or HNC $g_2(x)$ (solid lines) [13]. The inset compares the compressibility (pressure derivative, dashed lines) to the structure factor at the origin $S(k \to 0)$ (symbols), measured using a direct Fourier transform of the particle positions for small k and extrapolating to $k = 0$. (*Bottom*) The shear viscosity at high and low densities (inset), as measured using an externally-forced Poiseuille flow. There are significant rarefaction corrections for large mean free paths (i.e., at low densities and low collision rates).

in detail in Ref. [3]. The collision rules between solvent and solute particles is modified to provide a no-slip condition at the surface of the suspended sphere [3, 14] (slip boundaries give qualitatively identical results). For simplicity, we neglect rotations of the suspended sphere. For comparison, we also employ as a solvent an ideal fluid simulated using the M-I-DSMC algorithm, where we chose the collision rate so as to match the viscosity of the SHSD solvent.

The linearized (fluctuating) time-dependent compressible Navier-Stokes (NS) equations have been used to theoretically calculate $C(t)$ [14]. The results are analytically complex even in the Laplace domain, however, at short times an inviscid compressible approximation applies, and at large times the compressibility does not play a role and the incompressible NS equations can be used. During an initial transient period up to time $t_c = 2R/c_s$ sound waves are generated by the motion of the particle and distribute a fraction of the momentum of the suspended sphere to the surrounding fluid, so that the VACF quickly decays from its initial value $C(0) = kT/m$ to $C(t_c) \approx kT/M$, where $M = m + 2\pi R^3\rho/3$. After that the VACF decay

is as in an incompressible fluid, with a characteristic viscous timescale $t_{visc} = 4\rho R_s^2/3\eta$ and an asymptotic power-law tail $C \sim (kT/m)(8\sqrt{3\pi})^{-1}(t/t_{visc})^{-3/2}$, where we will approximate the effective (hydrodynamic) colloid radius as $R_s \approx R + D/8$.

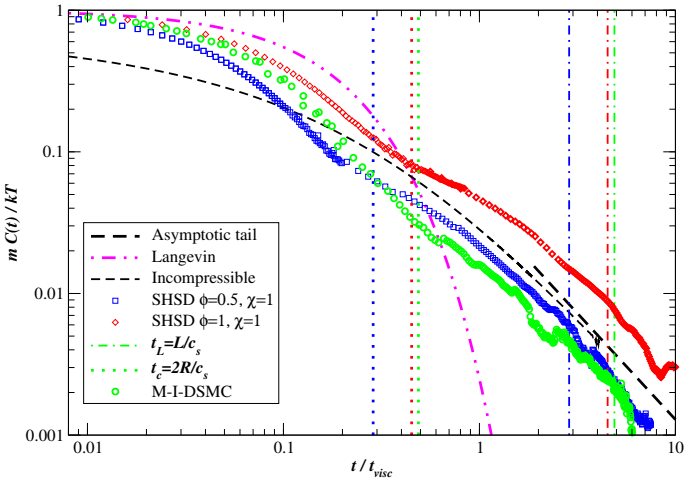

Figure 3: The velocity autocorrelation function for a neutrally buoyant hard sphere suspended in an SHSD fluid, as well as a fully compressible M-I-DSMC fluid, compared to predictions based on incompressible Navier-Stokes theory at short and long times. The diameter of the nano-colloidal particle is only $2.5D$, although we have performed simulations using larger spheres as well with very similar results. Since periodic boundary conditions were used we also show the time at which sound waves generated by its periodic images reach the particle, $t_L = L/c_s$, in addition to $t_c = 2R/c_s$. Compare to Fig. 13 in Ref. [14], obtained using MPCD for the solvent.

In Fig. 3 we show numerical results for the VACF along with the theoretical results in the incompressible limit. It is seen from the figure that the compressibility, i.e, the sound speed c_s, only affects the very early decay of the VACF. The slow decay at large times is seen even for the fully compressible fluid and is in qualitative agreement with the hydrodynamic predictions, but in sharp disagreement with predictions based on the Langevin equation (and thus Brownian dynamics). The coefficient of the VACF tail (i.e., t_{visc}) does not agree with the theory, likely because the sphere size is not much larger than the mean free path and thus there are significant corrections to the no-slip Navier-Stokes theory [14].

We have successfully designed a thermodynamically-consistent DSMC-like algorithm for non-ideal (dense) fluids. Unfortunately, for reasonable values of the collision frequency and density the SHSD fluid is still relatively compressible compared to a dense liquid. Indicative of this is that the diffusion coefficient is large relative to the viscosity, so that the Schmidt number $S_c = \eta(\rho\zeta)^{-1}$ is less than 10 instead of being on the order of 100. This is similar to DPD and comes because of the weakly repulsive potential. Achieving higher compressibility requires high collision rates and thus a similar relative increase in computational effort as in EDMD. The advantage of SHSD is its simplicity, easy parallelization, and easier coupling to continuum solvers. Future work will focus on improving the efficiency by reducing the rejection rate as well as coupling SHSD to a fluctuating hydrodynamics solver.

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